JOURNAL OF MATERIALS SCIENCE **37** (2002) 1831 – 1837

Tape casting aqueous alumina suspensions containing a latex binder

YONGHENG ZHANG
Department of Materials Science and Technology, Qingdao Institute of Chemical Technology, P.O. Box 64, No. 53 Zheng-Zhou Road, Qingdao 266042, People's Republic of China

J. BINNER
IPTME, Loughborough University, Leicestershire, LE11 3TU, UK

The tape casting of ceramic membrane substrates of ~1 mm thickness has been studied using two grades of ammonium polymethylacrylate (PMA) as a dispersing agent, dibutylphthalate as a plasticizer and polyvinylacetate (PVAc) latex as a binder. The colloidal stability of the alumina particles in the precursor slip was characterized using zeta potential measurements and the rheological behaviour of the slips. After tape casting, the density, strength and flexibility of the green tapes were studied in terms of changes in the plasticizer concentration and pH of the slip. The results indicated that alumina particles could be stabilized at pH 6–10 at a PMA15 concentration of 10 mg g^{-1}. The slips prepared with the polyelectroyte also displayed a strong shear thinning effect, which is important for tape casting. With the proper addition of plasticizer and adjustment of pH, it was found that a PVAc latex-based system can yield green alumina tapes with high green strength and flexibility.

1. Introduction

The doctor-blade tape casting technique is widely used in the electronics industry for the production of packaging materials [1, 2] and remains the best method for forming large area, thin, flat ceramic parts such as substrates [3, 4]. In the process, a suspension of ceramic powder is cast onto a moving carrier surface. The slip passes beneath the knife-edge of a blade that spread the slip into a layer of controlled thickness and width as the carrier surface advances along a supporting table. When the suspending medium is removed by evaporation, the ceramic particles coalesce into a relatively dense, flexible, green film that can be stripped from the carrier in a continuous sheet.

The ceramic suspension consists of a liquid medium containing the ceramic powder, dispersing agents, binders and plasticizers. The dispersing system [5] (liquid medium and dispersing agent) are selected to produce the desired viscosity in the slip for casting, whilst the binding system [6] (binders and plasticizers) are present to provide a high green strength after drying, allowing handling. It is thus essential that the composition of the slip is optimised to provide both good rheological properties for casting and excellent mechanical properties in the green tape.

Homogeneous dispersion of the ceramic powders in a highly loaded suspension is required to obtain reliable production of high quality products via tape casting. In general, suspensions may be stabilized by electrostatic, steric or electrosteric mechanisms [7, 8]. Electrostatic stabilisation is achieved by generating a common surface charge on the particles that are therefore repelled from one another. Steric stabilisation, on the other hand, is accomplished by adsorption of polymers onto the ceramic particle surfaces, the molecular chains acting as a barrier to prevent the particles from agglomerating. Electrosteric stabilisation is a combination of the two previous approaches and requires the adsorption of a layer of polymer that has long chains containing electric charges. Besides the nature of the ceramic powder and type of dispersant selected, the main factors affecting the efficiency of the stabilisation process in an aqueous media are the dispersant concentration, its molecular weight, and the system temperature and pH [9, 10].

The slips used for tape casting can be classified into aqueous- and non-aqueous-based systems; there are advantages and disadvantages associated with each. Organic-based systems can be formulated to use a variety of binders that yield excellent green tape strengths [11–13]. In addition, they generally have low boiling points so drying times can be short and productivity high. However, they do necessitate special precautions concerning toxicity and flammability. Whilst water-based slips are therefore generally considered attractive in terms of toxicity, environmental protection and price, their principle limitation is that it can be very difficult to achieve a suitable compromise between the required binder loading and the subsequent slip rheology. Whilst a high binder content is necessary to maintain the mechanical integrity of the green sheet during cutting, punching, and lamination, a high concentration of a water soluble binder such as PVA and cellulose can result in a high viscosity slip that is difficult to tape cast [14, 15]. In recent years, several authors have studied the use of aqueous-based acrylic emulsions as binders for preparing slips [16–18]. The colloidal properties of polymer emulsions specifically developed for ceramic applications can be used to prepare an aqueous-based slip with a high solid content and low viscosity. Moreover, these emulsions have useful and unique characteristics such as internal plasticisation and controllable crosslinking [19]. However, whilst such crosslinked polymers provide good mechanical strength in the green tape, they often display a low strain-to-failure. In order to produce a green tape with good flexibility, a plasticizer is usually employed to lower the glass transition temperature of the emulsion binder.

In the present work an aqueous-based system utilising PVAc latex as a binder and a polyelectrolyte dispersing agent has been studied for tape casting alumina substrates. The rheology of the slip was characterized using measurements of zeta potential and viscosity and the mechanical properties of the green tapes were studied with respect to changes in the plasticizer concentration and pH of the slips.

2. Experimental

2.1. Materials

The experimental materials were commercial products used without additional treatment. The alumina powder was A16SG supplied by Alcoa, USA. It had an average particle size of ~0.6 μm. The binder used was a 50 wt% solid content polyvinylacetate (PVAc) latex, Sitol 10 S 43, which was supplied by Kiilto Ltd, Finland. The latex was stabilized using ammonium polymethylacrylate and cellulose at pH 7.6. The particle size of the latex was ~1 μm according to the supplier. The dispersants used for the alumina were two grades of ammonium polymethylacrylate (PMA). These had molecular weights of 2000 and 15000 (denoted as PMA2 and PMA15 respectively) supplied by Aldrich Chemical Ltd, USA. The latter also supplied the plasticizer, dibutylphthalate (DBP, viscosity 0.2 Pa · s at shear rate 20 s^{-1}), and other chemicals, which included KNO_3, KOH and HCl solutions. The liquid medium was deionized water.

2.2. Slip preparation and characterisation

A Zetasizer4 (Malvern Instruments Ltd, UK) was used to measure the zeta potential of the alumina powder in the deionized water containing three levels of KNO_3 as an electrolyte to determine the point of zero charge (PZC) and, separately, with 2 to 14 mg g^{-1} of the two dispersing agents. A standard solid content of 1 wt% was used; the pH of the suspensions being controlled using 0.1 and 1 M KOH and HCl solutions. After pH adjustment, all the suspensions were dispersed using 45 W of ultrasonic energy for 2 minutes using a 400 W ultrasonic probe (Kerry Ultrasonic Ltd, England). Then the suspensions were centrifuged (C32-800, Philip Harris Ltd, UK) for 10 minutes at 2000 rpm to let all particles settle down and the equilibrium supernate carefully removed into a glass bottle. Only a very small portion of the sediment was then returned to the supernate to form the very dilute suspension as measuring sample.

Based on the above analysis, the alumina powder was added to deionized water containing the different levels of the two dispersants to generate slips with a solid content of 75 wt%. The suspension was mixed by ball milling for 24 hours before being used for further experiments. In cases of high viscosity, the agitation ball milling was used.

One series of samples, with different PMA2 and PMA15 concentrations, was used to study the effect of dispersant concentration and structure on the rheological behaviours of formed slips. A second series of samples, without the addition of plasticizer, was used to evaluate the effect of the latex binder on the rheological behaviour of the slip. Sufficient latex solution was added to the slip to yield a latex content varied from 0 to 20 wt% (solid content) and mixed in using a further 2 hours of ball milling. In a third series of experiments, the pH of the slip with and without the latex binder was altered using 1 M KOH or HCl solution in order to evaluate the effect of pH on the rheological behaviour of the slip and the subsequent green tape properties. In each case, the viscosity of the slips was measured using a Bohlin Visco88 viscometer (Bohlin Ltd, Sweden). After obtaining a steady state viscosity over 10 s at an initial shear rate of 18 s^{-1}, the shear rate was swept up to 334 $^{-1}$ and back down again.

After the viscosity measurements were complete, the slips were cast on a polyethylene terephthalate film using a tape casting machine (Cerlim Equipment, Limoges, France). In each case the slips had an alumina content of 60 wt%, 10 mg g^{-1} of PMA15 as the dispersing agent and a fixed binder content of 10 wt%. The plasticizer concentration was varied from 0 to 40 wt% of the binder content in intervals of 5 wt%. The casting speed was kept constant at 1.2 cm s^{-1} and the thickness of the casting was controlled at 1.2 mm. All the castings were performed at room temperature of about 20°C. The green tape was allowed to dry at room temperature for 40 hours before removed from the film. The green tape was then dried in an oven at 80°C for 2 hours before characterisation. The mechanical strength and strain-to-failure was evaluated via tensile testing using a cross-head speed of 2 mm min^{-1} (M30K, J.J. Lloyd Instrument Ltd, UK). The green tape density was measured using the Archimedes technique using mercury whilst the green microstructures of tapes with plasticizer contents of 12 wt% and 40 wt% were evaluated using scanning electron microscopy (JSM-6400, Jeol Ltd, Japan).

3. Results and discussions

3.1. Powder dispersion and slip preparation

Fig. 1 shows the change in zeta potential for the alumina particles in three different KNO_3 solutions as a function of pH. The point where all three isotherms cross one another can be identified as the point of zero charge (PZC) because only at that point is the surface charge independent of the concentration of the supporting electrolyte KNO_3. It can be seen that the PZC of the alumina was about 8.6. This is consistent with the values of 8 to 9 reported by other authors [20].

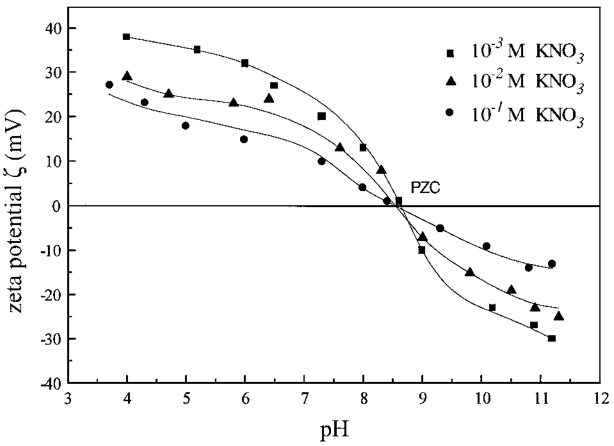


Figure 1 Variation in zeta potential with pH at different electrolyte concentrations for A16SG alumina powder.

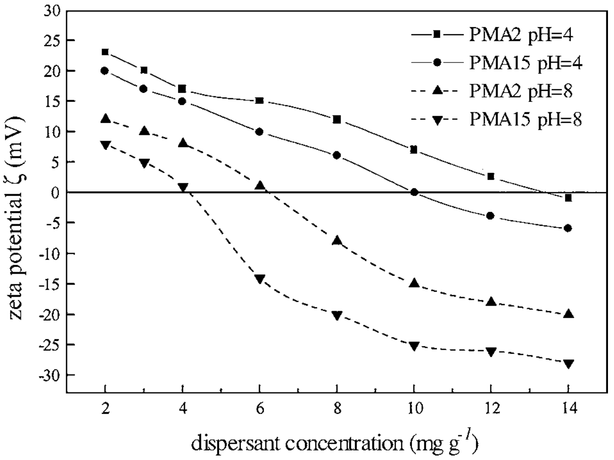


Figure 2 Variation in zeta potential as function of dispersant concentration for A16SG alumina powder.

The effects of the two polyelectrolytes, PMA2 and PMA15, on the zeta potential are shown in Fig. 2. At a pH of 4 both dispersants had a weak effect on the zeta potential and about 14 and 10 mg g^{-1} respectively were required to shield the surface charge. However, at the higher pH of 8 the charge developed on the alumina was smaller and hence consequently less polyelectrolyte was required to shield it, only about 6 and 4 mg g^{-1} respectively. It is well known that many factors can affect the adsorption affinity of a given dispersant on a ceramic particle, including pH and temperature [9, 20, 21]. For example, Cesarano *et al.* [9, 10] reported that the quantity of polymethacrylate required for monolayer polymer coverage of alumina particles, and hence complete electrosteric dispersion, decreased with increasing pH. This was attributed to the dominance of a loop and tail configuration at low pH, whilst at higher pH values up to the ceramic's PZC, the presence of a train configuration of stretched negatively charged polymer adsorbed onto positively charged surface sites was considered to exist. At pH values above the PZC, electrostatic repulsions between the negative powder and negative polymer caused the linear polyelectrolyte to dangle into the solution, adsorbing to the surface only at the few minor regions of positive surface charge. This model has been supported by Tjipangandjara *et al.* [22] who studied the configuration of adsorbed polyacrylic acid on alumina from solutions of fixed and varying pH using fluorescence spectroscopy techniques. The difference in performance between the two polyelectrolytes may be explained by their differences in molecular weight since both will have carried the same charge. PMA2, with the lower molecular weight, has shorter chains that will be less effective for steric dispersion.

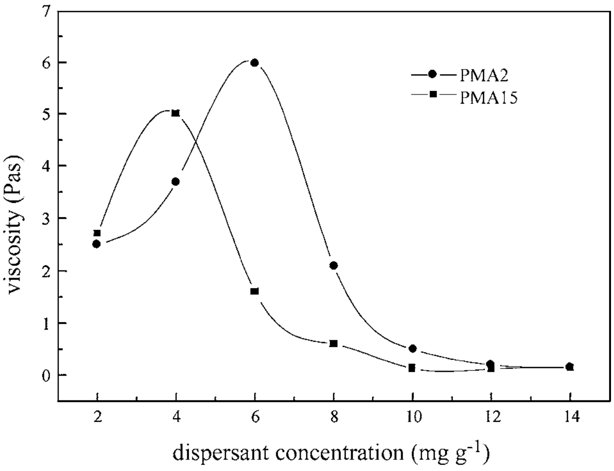


Figure 3 Variation in viscosity with dispersant concentration for the alumina slips. The pH of the slips was 8.7 and the viscosity was measured at 18 s^{-1} with an increasing shear rate.

Fig. 3 shows the change in viscosity as a function of dispersant concentration at a shear rate of 18 s^{-1} and using a pH of 8. The maxima in the curves correspond very well with the values for the isoelectric points found from Fig. 2 at 6 mg g^{-1} and 4 mg g^{-1} for PMA2 and PMA15 respectively. At these points the electrostatic contribution to dispersion will have been lost and the mechanism will be purely from the steric effect of the adsorbed dispersants. The suspension will therefore be at its most flocculated. As a result of its lower molecular weight and shorter chains, the PMA2 led to a higher viscosity for the suspension than with the PMA15 dispersant. The minimum viscosity observed for slips dispersed with PMA2 and PMA15 occurred at concentrations of 12 mg g^{-1} and 10 mg g^{-1} respectively. This result is consistent well with the zeta potential measurement shown in Fig. 2 that at these concentrations, the adsorption of polyelectrolytes and surface zeta potential reached saturation. According to this study, the PMA15 displayed more effective in dispersing Al_2O_3 powder in aqueous media and was selected to evaluate in later experiments.

The flow properties of the slips prepared with PMA15 at different concentrations are listed in Table I. The data listed in the first column, η_{18I}, is the same as that shown for the PMA15 curve in Fig. 3. The background to the remaining data is described in the notes under the table. The value η_{18I}/η_{18D}, usually referred to as a thixotropic index, increased with dispersant concentration up to the value of 10 mg g^{-1}. Thus at low concentrations of dispersant, when the slip was agglomerated as a result of charge neutralisation and the viscosity was high, the attractive forces between the particles were sufficiently strong to reform within a very short time after shearing. The viscosity measured at 18 s^{-1} on the downward sweep was thus essentially the same as that measured

TABLE I Flow properties of the alumina slip as a function of different dispersant concentrations

Dispersant (mg g^{-1})	Viscosity (Pa s)				
	η_{18I}	η_{18D}	η_{334}	η_{18I}/η_{18D}	η_{18I}/η_{334}
0	2.70	2.65	1.78	1.02	1.51
4	5.00	4.8	3.10	1.04	1.61
6	1.60	1.45	0.70	1.10	2.28
8	0.60	0.51	0.30	1.17	2
10	0.13	0.10	0.08	1.30	1.6
12	0.14	0.10	0.08	1.21	1.75

Subscripts without brackets refer to the shear rate and whether it was increasing (I) or decreasing (D), e.g. η_{18I} represents the viscosity measured at a shear rate of 18 s^{-1} when the shear rate was increasing during measurement.

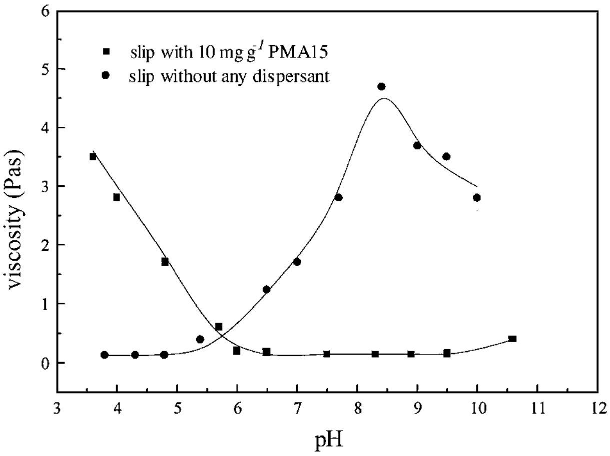


Figure 4 Changes of viscosities for slips dispersed with and without dispersants as a function of pH.

on the upward sweep at the same shear rate and the thixotropy index was essentially 1. However when the degree of dispersion was increased, the interaction between the particles was too weak to reform rapidly and the thixotropic index increased. The shear thinning effects of the slips increased with dipsersant concentration and then started to decrease slightly after PMA15 concentration of 10 mg g^{-1}. The shear thinning behaviour of slips is desirable for tape casting, especially for casting of substrate up to 1.0 mm in thickness. Rapid increase in viscosity after high shearing will prevent continuous spread of the slip, so the green tape will have good thickness distribution along cross sections of the tape.

The effect of pH on the rheological behaviours of the slips (75 wt%) can be seen from Fig. 4. When there was no dispersant used, the slip had low viscosity as pH was below about 5. The viscosity increased until pH about 8.5, then started to decrease slightly. The increase of viscosity indicated the agglomeration of particles in the slips as a result of reduction in surface zeta potentials and at pH about 8.5, near the isoelectric point as shown in Fig. 5, the viscosity reached its maximum. This result clearly demonstrated that when the particles were dispersed with purely electrostatic interaction the particles were stable only in a strong acidic environment which requires to add significant amount of acid. When the slip was dispersed with PMA 15, the slips exhibited low viscosity at pH 6–10. The viscosity increased significantly as pH decreased from 6. The slip had a pH of 8.5 before any pH adjustment. Nevertheless, a maximum viscosity was not observed at i.e.p where the surface charges was zero, so was the electrostatic force. This result could be explained by the presence of absorbed polymer PMA15 on the particle surface which provided the steric force between particles. Even though the adsorption of PMA15 decreased with increasing pH of the suspension the steric effect, as well as the electrostatic effect from each molecule adsorbed on the particle surface should increase. Hence, the overall repulsion force between particles needs to be optimised by considering the contributions from the electrostatic and steric effects. It was found from this study that the 75 wt% solid content slip was stable in the pH range 6–10 with a PMA15 concentration of 10 mg g^{-1}. The pH range for a stable dispersion system is expected to decrease with increasing solid loading as the average distance between particles decreased, whilst the Van der Waals force between particle increased. Consequently, a higher threshold force was required to prevent the particles from agglomeration.

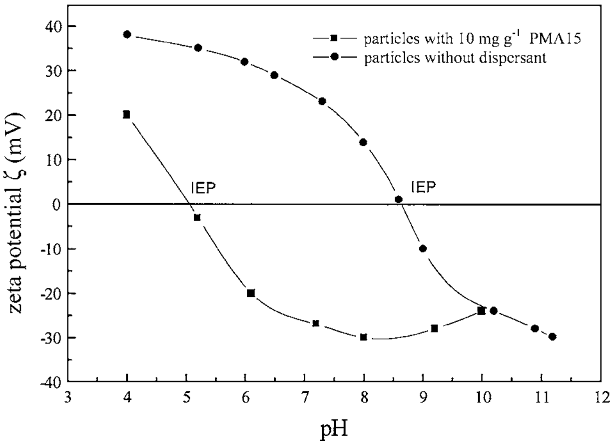


Figure 5 Changes of zeta potentials for alumina particles with and without presence of dispersant as a function of pH.

In order to understand the effect of binder content on the rheological behaviour of the slip, the changes in viscosity with binder contents were measured at pH 8 as shown in Fig. 6. Although there is a slight increase

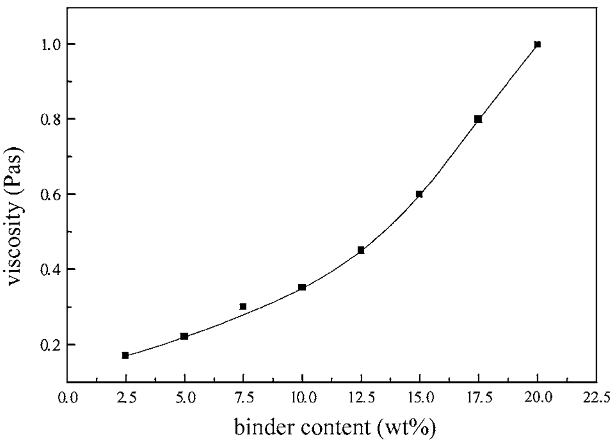


Figure 6 Variation in alumina slip viscosity as a function of binder content (alumina content 60 wt%; 10 mg g^{-1} PMA15; pH 8).

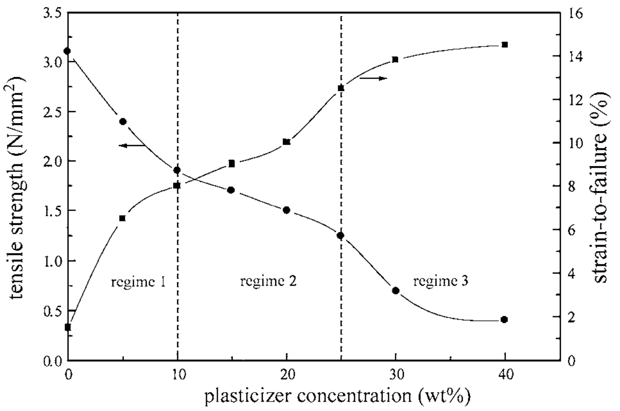
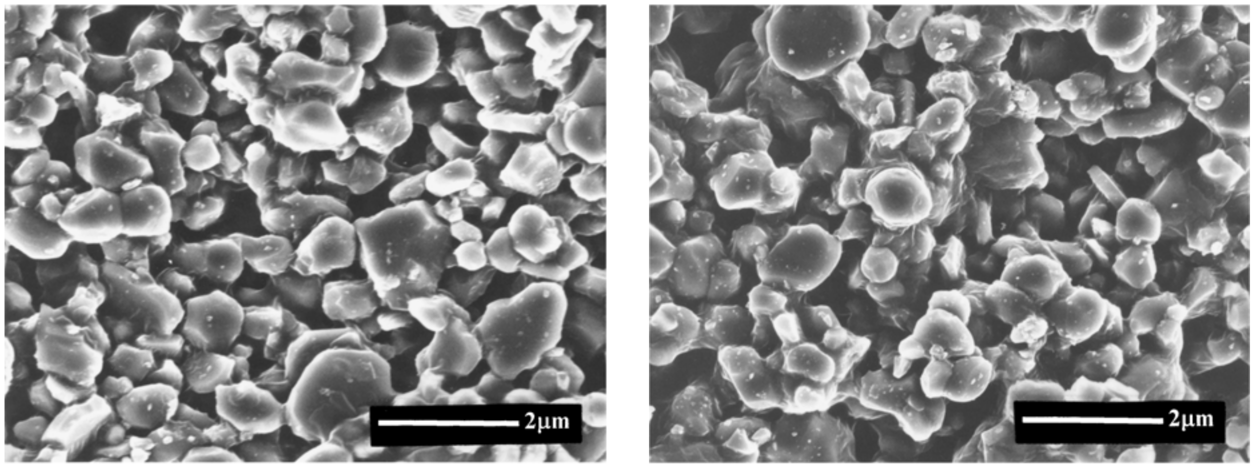


Figure 7 Variation in tensile strength and strain-to-failure of the green tapes as a function of plasticizer concentration.

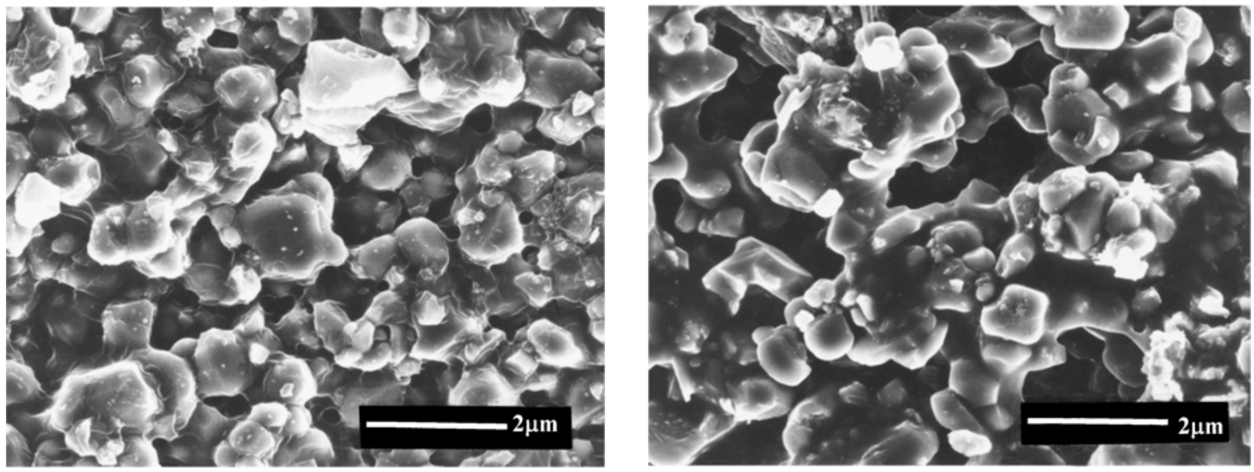
in viscosity increase at binder contents above approximately 12.5 wt%, nevertheless there was no fundamental change in shear thinning rheological behaviour. This suggests that there was no significant interaction between the latex particles and alumina particles. This is possibly attributable to the fact that the same dispersant was used to stabilize both the alumina and latex particles. It was also noted that the addition of plasticizer in quantities up to 40 wt% of the latex content caused a slight reduction in viscosity of ∼10% but again no significant change in rheological behaviour of the slip.

3.2. Characterisation of green tapes

Fig. 7 shows the maximum rupture strength and strain-to-failure of the green tapes as a function of plasticizer concentration. Three separate regimes have been identified. In the first, up to plasticizer concentrations of ∼10 wt%, there is a sharp reduction in strength and increase in strain-to-failure. It is believed that the decrease in strength resulted from the insertion of the plasticizer molecules inside the macromolecular network formed by the binder [12]. This will have destroyed the local intermolecular strength responsible for the mechanical cohesion of the compound. As a result the strength of the tape decreased significantly, even with addition of small amounts of plasticizer, whilst at the same time the strain-to-failure was greatly improved. In the second regime, which covered the approximate range 10–25 wt% plasticizer, both the strength and strain-to-failure changed more gradually with increases in the plasticizer concentration. This supports the idea that whilst most of the plasticizer molecules interlinked with the binder molecules, they also began to form a separate phase [23]. At concentrations above about 25 wt%, the

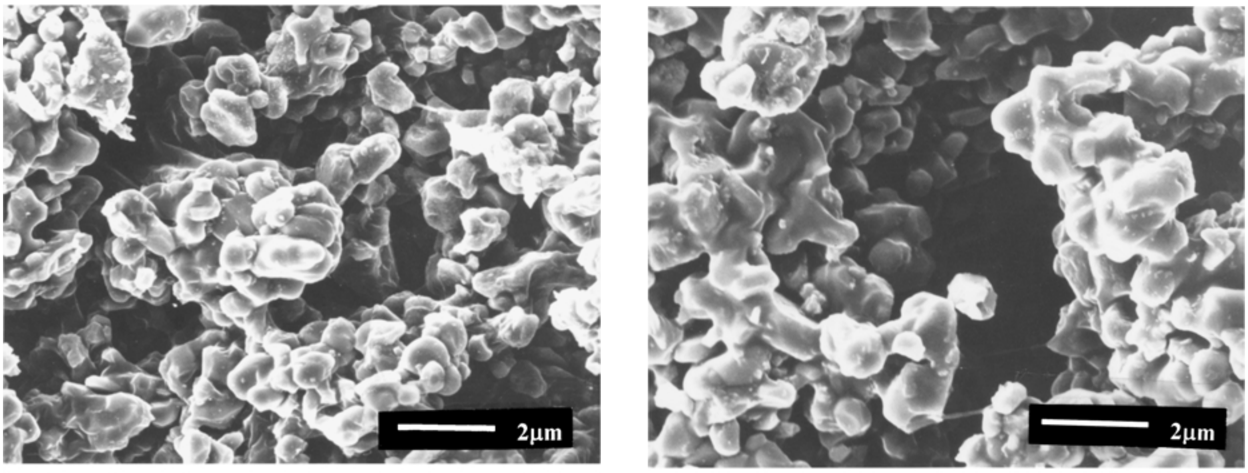


(a) Tape surface (b) Fracture surface



(c) Tape surface (d) Fracture surface

Figure 8 The microstructure of tapes cast with a plasticizer content of 12% (a and b) and 40% (c and d).



(a) Tape surface

(b) Fracture surface

Figure 9 The microstructure of the tape cast at pH 5.

third regime, the excess plasticizer would be present as a discrete, separate phase causing a significant reduction in the strength of the green tape but improving the strain-to-failure of the tape very little due to the formation of voids in the green tapes.

Fig. 8a and b show micrographs of the tape surface and a fracture surface of the cross-section of a dry green tape produced with a plasticizer concentration of 12 wt%. An homogenous distribution of the particles may be observed. When the plasticizer content was increased to 40 wt%, large voids were found both on and inside the tape, as shown in Fig. 8c and d. These voids are thought to be a result of residual plasticizer that did not interact with latex but remained as a separate phase as outlined above. This suggestion is based on the physical properties of the plasticizer used, DBP. It has a water solubility of <1 mg g^{-1}. Therefore, most of free DBP could exist in the slip as small droplets that would coalesce to form larger ones during the drying process.

In order to investigate the stability of the tape casting system with respect to slip pH, the latter was altered prior to casting using 1 M KOH and HCl without making any other changes to its composition. The consequences on the viscosity, green tape density, strength and strain-to-failure are shown in Table II. It was found that the slip system was reasonably stable over the pH range 6 to 10, with no significant variation in either slip viscosity or subsequent tape properties over the range 8 to 10. At low pH values the slip became flocculated and the viscosity increased sharply as expected based on the earlier work. Difficulties were experienced with casting and the microstructure produced contained significant defects, Fig. 9. As a consequence, the density of the green tape was low and the mechanical properties poor.

TABLE II The effect of pH on the properties of the green tapes formed

pH	η_{18F} (Pa s)	ρ (g cm^{-3})	Strength (N mm^{-2})	Strain-to-failure (%)
4	4.80	1.88	1.07	3.0
5	3.21	2.01	1.18	4.7
6	0.42	2.39	1.64	8.8
8	0.35	2.48	1.70	9.0
10	0.37	2.42	1.68	9.0

4. Conclusions

A tape casting system suitable for production of alumina tapes and based on using a latex binder has been developed. Two different aspects related to the process were investigated, viz. slip preparation and the tape casting itself.

Ammonium polymethacrylate has been confirmed to be a suitable dispersing agent for alumina particles in an aqueous medium and the effect of both pH and molecular weight has been investigated. A pH of approximately 8–10 is optimum for the electrostatic part of the dispersion mechanism, whilst a higher molecular weight improves the effect of the steric part of the mechanism. The slip prepared with PMA15 also exhibited a strong shear thinning effect which allowed a rapid build up of viscosity after casting.

It was also observed that the use of a PVAc latex binder allowed the production of slips that displayed a low viscosity even with relatively high binder contents. This could be a major advantage for tape casting. The mechanical properties of the ensuing green tape could be varied by adjusting the plasticizer concentrations; the optimum level of DBP was found to be 12 wt%. This yielded tapes which exhibited high green strength but which were also flexible enough to survive handling and subsequent operations.

References

1. R. E. MISTLER, *Am. Ceram. Soc. Bull.* **69**(6) (1990) 1022.
2. E. M. ANDERSON, R. A. MARRA and R. E. MISTIER, *ibid.* **76**(7) (1997) 45.
3. C. SIMON, R. BREDESEN, H. RAEDER, M. SEIERSTEN, A. JULBE, C. MONTELL, I. LAAZIZ, J. ETIENNE and L. COT, *Key Engineering Materials* **61/62** (1991) 425.
4. M. W. MURPHY, T. R. ARMSTRONG and P. A. SMITH, *J. Amer. Ceram. Soc.* **80**(1) (1997) 165.
5. S. SUMITA, W. E. RHINE and H. K. BOWEN, *ibid.* **74**(9) (1991) 2189.
6. R. MORENO, *Am. Ceram. Soc. Bull.* **71**(11) (1992) 1647.
7. T. F. TADROS, *L'actualitκ chimique* **9** (1987) 270.

8. D. H. NAPPER, in "Polymeric Stabilization of Colloid Dispersions" (Academic Press, London, 1983) p. 10.
9. J. CESARANO III and I. A. AKSAY, *J. Amer. Ceram. Soc.* **74**(4) (1988) 250.
10. *Idem.*, *ibid.* **71**(12) (1988) 1062.
11. R. MORENO, *Am. Ceram. Soc. Bull.* **71**(10) (1992) 1521.
12. M. DESCAMPS, G. RINGUSET, D. LEGER and B. HIERRY, *J. Euro. Ceram. Soc.* **15** (1995) 357.
13. T. CHARTIER and A. BRUNEAU, *ibid.* **12** (1993) 243.
14. N. KIRATZIS and P. F. LUCKHAM, *ibid.* **8** (1998) 783.
15. C. PAGNOUX, T. CHARTIER, M. F. GRANJA, F. DOREAU and J. M. FERREIRA, *ibid.* **18** (1998) 241.
16. N. USHIFUSA and M. J. CIMA, *ibid.* **74**(10) (1991) 2443.
17. K. NAGATA, *J. Ceram. Soc. Japan* **101**(8) (1993) 845.
18. N. R. GURAK, P. L. JOSTY and R. J. THOMPSON, *Am. Ceram. Soc. Bull.* **66**(10) (1987) 1495.
19. A. FOISSY, A. E. ATTAR and J. M. LAMARCHE, *J. Colloid Interface Sci.* **96**(1) (1983) 275.
20. L. GUO, Y. ZHANG, N. UCHIDA and K. UEMATSU, *J. Euro. Ceram. Soc.* **17**(2–3) (1997) 345.
21. K. F. TJIPANGANDJARA, Y-B. HUANG, P. SOMASUNDARAN and N. J. TURRO, *Colloids and Surfaces* **44** (1990) 229.
22. A. DINSDALE and F. MOORE, in "Viscosity and its Measurement" (Chapman and Hall Ltd, London, 1962) p. 45.
23. B. SAKELLARIOU, H. HASSAN and R. C. ROWE, *European Polymer Journal* **29**(7) (1993) 937.

Received 30 March
and accepted 11 December 2001